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(54)   **Process for the conversion of methane to synthesis gas**
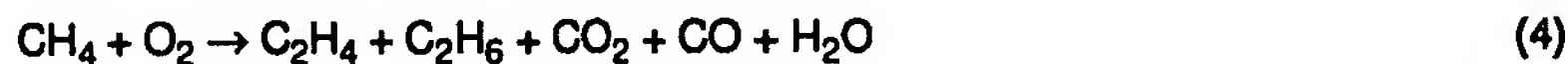
(57)   A method of converting a reactant gas mixture
of CO_2, O_2 and CH_4 comprises contacting the reactant
gas at 750 - 850°C with a solid catalyst, which is a d-
block transition metal or oxide such as a group VIII
metal on a metal oxide support such as alumina, and
which selectively converts the reactant gas into a prod-
uct gas mixture comprising H_2 and CO.

EP 0 780 339 A2

Description

In view of the dwindling supplies of fossil fuels and the relative abundance of methane, there is considerable interest in processes which hav greater efficiency and selectivity for the conversion of methane t synthesis gas. There are several known reactions for the oxygenation of methane.

There are several known reactions for the oxygenation of methane.

$$CH_4 + O_2 \rightarrow CH_3OH \tag{1}$$

$$CH_4 + O_2 \rightarrow CO + H_2 \tag{2}$$

$$CH_4 + O_2 \rightarrow CH_2O + H_2O \tag{3}$$

$$CH_4 + O_2 \rightarrow C_2H_4 + C_2H_6 + CO_2 + CO + H_2O \tag{4}$$

$$CH_4 + O_2 \rightarrow CO_2 + H_2O \tag{5}$$

The partial oxidation of methane by dioxygen to synthesis gas, according to the stoicheiometry:

$$CH_4 + 1/2 \, O_2 \rightarrow CO + 2 \, H_2 \qquad \text{Equation (2)}$$

is an exothermic reaction, for which the values for ΔH and ΔS at 298 K are[1] -36 kJmol[-1], and +170 JK[-1]mol^{-1}, respectively, and for which ΔG = -215 kJmol[-1] at 1050 K.

There are also catalysts for the reforming of methane using carbon dioxide:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{6}$$

This reduction of carbon dioxide by methane is an endothermic reaction[1] (ΔH_{298} = +247 kJmol[-1]). At high temperatures. its favourable entropy change (ΔS_{298} = +257 JK[-1]mol^{-1}) makes it a favourable equilibrium, ΔG = -23 kJmol[-1] at 1050 K.

Different catalysts promote these reactions to different extents, but selectivity is normally poor. This patent application results from our discoveries of a class of catalysts that is capable of selectively reforming methane to carbon monoxide and hydrogen according to equation (6) and a class of catalysts capable of combining both the partial oxygenation reaction shown in equation 2 with the reforming reaction shown in (6).

The major commercial process for the utilization of methane (steam reforming) involves a nickel catalysed reaction of methane with steam.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
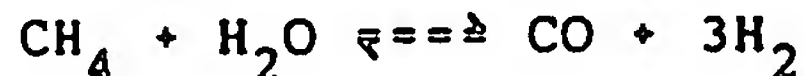
The products of this reaction are four gases which under catalytic conditions are in the equilibrium known as the water-gas shift reaction, namely

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
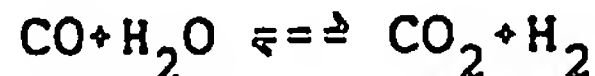
The equilibrium concentrations depend on the temperature and pressure at which the catalytic reaction is carried out.

The two gases, carbon monoxide and hydrogen, can be combined under catalytic conditions to give useful chemicals such as methanol or , via Fischer-Tropsch catalysis, higher hydrocarbons or aldehydes and alcohols. In consequence, the steam r forming process is an important industrial source of carbon monoxide and hydrogen, but the technology of steam conversion requires considerable capital investment, and is relatively inefficient since water and carbon dioxide are unwanted by-products of the reacti n.

Therefore there is considerable industrial interest in the combined reforming-partial oxidation of methane to give

carbon monoxide and hydrogen as the substantially major products.

British Patent Application N . 9018781.6 describes the catalysts for the partial oxidati n of methan by oxygen to synthesis gas under relatively mild conditions of 650-900°c and pressures of 10-600 KPa without the use of steam. The catalysts include d-block transition metals on a refractory support and d-block transition metal oxides including mixed metal oxides.

Thus, this invention is concerned with essentially two processes. Process 1 is the reaction of CO_2 with methane giving synthesis gas according to Equation 6. Process 2 is the reaction of oxygen and carbon dioxide mixtures with methane also giving synthesis gas.

$$(a)CO_2+(b)O_2+(c)CH_4 \rightarrow (x)CO+(y)H_2$$

A potential application of reaction 6, which is endothermic, is to use energy such as solar energy to drive the reaction to form the synthesis gas, which could then be stored and transported. The reverse reaction, namely the reduction of CO to methane, for which there are well-known catalysts, is highly exothermic thus heat stored by the first reaction can be released by the reverse methanation.

Another aspect of the invention concerns the potential application for usage of CO_2, which has environmental implications towards the general problem of the greenhouse effect.

This invention is concerned with the definition of the conditions and catalysts which will give rise to the conversion of the methane and CO_2, O_2 to synthesis gas with greatly improved selectivity and conversions. Accordingly, the present invention provides a method of converting a primary reactant gas mixture comprising CO_2, O_2 and CH_4 into a product gas mixture comprising H_2 and CO which method comprises bringing the primary reactant gas mixture at a temperature of from 600-1000°C into contact with a solid catalyst of the following formula:

$M_xM'_yO_z$ or M_xO_z or M'_yO_z or M' on a refractory support

where M is at least one metal selected from Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, B, Al, Sc, Y, Ln, Ga, In, Tl, Bi, U, Th and Pb.

Ln is selected from La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y.

M' is at least one metal selected from Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th and U.

Each of the ratios x/z and y/z and (x + y)/z is independently from 0.1 to 8, preferably from 0.5 to 0.75. The method is characterised in that CO_2 is a feedstock to the primary reactant gas mixture.

Alternatively, the metal oxide systems may be obtained from catalyst precursors, from which the active catalyst is formed by heating under non-oxidizing conditions. For example, the catalyst precursor may decompose to yield the metal on the oxide support.

All the metal oxide systems may be crystalline, monophasic or polyphasic, they may be amorphous, they may be stoichiometric or non-stoichiometric; they may have defect structures. They may be solid solutions. The values of x, y and z may be integral or non-integral. In the mixed metal oxides, the ratio of x to y is not critical and may for example be from 0.001 to 1000.

Catalyst preparation is normally straightforward: the metal oxides, or precursors thereof such as carbonates or nitrates or any thermally decomposable salts, can be precipitated onto a refractory solid which may itself be massive or particulate. Or one metal oxide or precursor may be precipitated onto the other.

Preferred catalyst precursors are those having M' highly dispersed on an inert metal oxide support and in a form readily reducible to the elemental state.

The combined partial pressures of the reactant gases should preferably lie in the range 0.01MPa - 10MPa, preferably at 0.1 MPa.

The reaction 6 is endothermic, H = +247 kJ and it is required to heat the reactant gases at temperatures in the range 600-1000°C. The ratio of CO_2 to methane may vary from 0.1 - 10. A preferred temperature range is from 750 to 850°C.

One advantage of using as a feed-stock gas a mixture of CO_2, O_2 and methane is to obtain an effectively thermal neutral reaction, and this can be achieved when the ratio of CO_2 to O_2 is approximately 1:6. Many natural sources of methane contain carbon dioxide.

The mole ratio of the reactant gases CO_2 and O_2 to CH_4 should be:CO_2 (a): O_2 (b): CH_4 (c=2b + a) , at ideal stoichiometry.

In a further aspect of the invention the reaction is carried out with an excess of CO_2 such that the ratio of a/c-2b > 1. Under these conditions of excess CO_2, the reaction

$$2CO \rightarrow C + CO_2$$

is suppressed; this allows the use f cheaper catalysts such as nickel. This is demonstrated in the data in Experiment 15 using a nickel catalyst. The excess CO_2 is largely converted (by the hydrogen generated) to CO by the reverse water

gas shift reaction

$$CO_2 + H_2 \rightarrow CO + H_2O$$

This gives excellent overall CO yields.

The reaction vessel containing the catalytic reaction should be made of an inert material for example inert oxides, such as quartz (SiO_2) or alumina, and containers such as steel are ineffective if they cause deposition of carbon.

We presently believe that the catalysts serve to achieve essentially thermodynamic equilibrium between all possible products according to the following equations:

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$$
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
$$CH_4 + CO_2 \rightleftharpoons 2CO + H_2$$
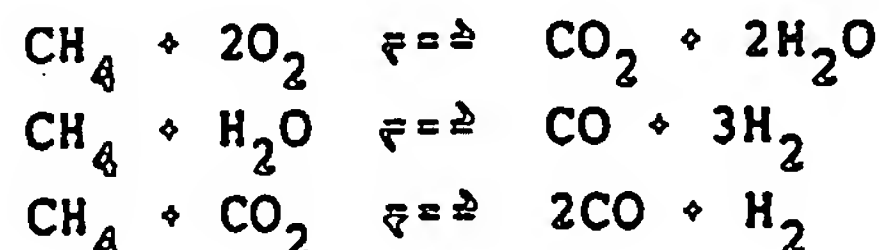
The selectivity shown towards the major and desired products, namely CO and H_2 reflect the thermodynamic equilibrium under the prevailing conditions. Computer simulations, based on minimizing the total free energy of all possible product combinations excluding carbon, (limited by stoichiometry, of course) predict very similar results to those we obtain, and we are thus confident that thermodynamic equilibrium is attained under our reaction conditions.

The present invention is further illustrated by the following examples in which the reaction 6,

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2,$$
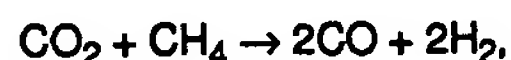
has been catalysed by a number of catalysts, as indicated in the data in experiments 1-8.

Experiments 1-6 show that man different transition metals can act as catalysts.

Experiments 1, 7, 8 show how the reaction conditions affect the products.

All the experiments were carried out using 50mg of solid, powdered catalyst, lightly packed between <20mg of silica wool (MULTILAB) in a straight silica reaction tube of i.d. ca. 4mm. The reaction tube (300mm) was placed in the vertical tube furnace of a LABCON microreactor and connected to a supply of the gas reaction mixture. The reactant gases, methane (supplied by Union Carbide, Gas and Equipment Ltd.), carbon dioxide (supplied by British Oxygen Company), dioxygen (supplied by Air Products) and dinitrogen (supplied by Air Products) were dried over molecular sieves and passed over the catalyst at a rate of 1-50 ml/min (GHSV of $0.12 - 7 \times 10^4$ hour^{-1}). The temperature of the reaction tube was raised from ambient to the required temperature (typically 1050K, unless otherwise stated) over a period of 2 hours. The reaction products were monitored using an on-line Hewlett-Packard 5890A gas chromatography apparatus. Separation of all gases was obtained using Helium carrier gas through Porapak Q and 5A molecular sieve packed columns, and were detected using a Thermal Conductivity Detector, calibrated on site. In all cases, O_2 conversion was >99.5%, and C, H, O, N mass balances were better than 96%.

Particulars for the catalytic reduction of CO_2 by CH_4. Mixtures of methane and carbon dioxide were passed over heterogeneous catalyst systems which were selected in the light of our previous experience with catalysts for the partial oxidation of methane. The conditions of the experiments and the products of the reactions are given in the Tables 1-8. These show that several of the catalysts under study are highly effective for the conversion of methane to synthesis gas operating under mild conditions of pressure, at 1050K, and with large gas hourly space velocities.

Particulars for the catalytic conversion of mixtures of CO_2, O_2 and CH_4 to synthesis gas.

Mixtures of CO_2, O_2 (or air) and CH_4 have been passed over selected heterogeneous catalysts. The conditions and products of the reactions are given in Tables 9-15. The data show that several of the catalysts studied are highly efficient for the conversion to synthesis gas. Extended catalyst life-time studies are in progress but, as indicated in Table 1 most catalysts should be expected to show no deterioration in activity after 80 hours, and possibly much longer.

<u>Experiment 1:</u> Results obtained over 50 mg 1% Ir/Al_2O_3, GHSV = 2×10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from $IrCl_3$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
3.84	100	41	70	54
2.96	99	50	76	62
1.99	97	62	83	74
1.00	88	91	87	89*
0.60	58	96	57	71
0.49	47	98	47	64
0.35	34	100	34	51

* This experiment ran for 80 hours with no observed loss of activity or selectivity.

Experiment 2: Results obtained over 50 mg 1% Rh/Al_2O_3, GHSV = 1.7 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from $RhCl_3$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
1.10	88	86	87	88
1.00	86	88	85	87

Experiment 3: Results obtained over 50 mg 1% Ru/Al_2O_3, GHSV = 1.9 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from an organometallic CpRu (PMe)$_3$ (B_4H_9), subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
1.05	67	71	62	69
0.92	58	73	53	65

Experiment 4: Results obtained over 50 mg 1% Pd/Al_2O_3, GHSV = 1.9 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from $PdCl_2$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
0.95	70	77	69	74
0.98	71	75	69	73

Experiment 5: Results obtained over 50 mg Ni/Al$_2$O$_3$, GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst ex-British Gas Plc., CRG 'F', 1/8" pellets, lightly crushed before use in the microreactor.

CO$_2$/CH$_4$	% CH$_4$ converted	%CO$_2$ converted	% yield H$_2$	%yield CO
0.98	88	81	88	85

Experiment 6: Results obtained over 50 mg 1% Pt/Al$_2$O$_3$, GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from PtCl$_2$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO$_2$/CH$_4$	% CH$_4$ converted	%CO$_2$ converted	% yield H$_2$	%yield CO
0.81	22.3	41.3	16.9	30.8
0.95	23.8	42.6	15.6	33.0
At GHSV 5 x 10^3 hour^{-1}				
0.97	71.9	84.6	66.9	78.2

Catalysts 1% Pd/Al$_2$O$_3$ and Ni/Al$_2$O$_3$ formed large amounts of carbon, gradually losing their activity and becoming totally clogged up with coke within a few hours.

Experiment 7: Results obtained over 50 mg 1% Ir/Al$_2$O$_3$, GHSV = 2 x 10^4 hour^{-1}, CO$_2$/CH$_4$ = 1.00, 0.1 MPa.

Temp K	% CH$_4$ converted	%CO$_2$ converted	% yield H$_2$	%yield CO
900	20	30	14	26
950	34	44	28	40
1000	59	68	54	64
1050	88	91	87	89

Experiment 8: Results obtained over 50 mg 1% Rh/Al$_2$O$_3$, 1050 K, CO$_2$/CH$_4$ = 1.00, 0.1 MPa.

GHSV hour^{-1}	% CH$_4$ converted	%CO$_2$ converted	% yield H$_2$	%yield CO
5 x 10^3	88	91	87	89
1 x 10^4	88	91	87	89
1.7 x 10^4	86	88	85	87
2.4 x 10^4	85	87	83	86
5.6 x 10^4	68	74	68	71

Experiment 9: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Ir/Al_2O_3, GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

O_2 conversions $\geq$ 99.7%

Feed Composition			% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
% CH_4	% CO_2	% O_2				
64.4	3.5	32.1	92	9	89	86
59.4	20.0	20.6	87	83	81	86
58.3	23.7	18.0	84	83	81	84
58.0	28.0	14.0	83	90	79	85
49.8	48.8	1.4	91	87	91	89

Experiment 10: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Pd/Al_2O_3, GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

O_2 conversions $\geq$ 99.7%

Feed Composition			% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
% CH_4	% CO_2	% O_2				
58.1	28.5	13.4	60	56	53	59

Experiment 11: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Ru/Al_2O_3, GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

O_2 conversions $\geq$ 99.7%

Feed Composition			% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
% CH_4	% CO_2	% O_2				
57.3	29.5	13.2	70	74	63	71
56.8	29.3	14.0	72	73	64	72

Experiment 12: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Rh/Al_2O_3, GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

O_2 conversions $\geq$ 99.7%

Feed Composition			% CH$_4$ converted	%CO$_2$ converted	% yield H$_2$	%yield CO
% CH$_4$	% CO$_2$	% O$_2$				
56.5	29.0	14.5	85	88	79	86
57.2	29.5	13.3	82	89	77	85*
56.2	28.5	15.3	88	90	83	89**

* GHSV = 4 x 10^4 hour^{-1}
** GHSV = 1.5 x 10^4 hour^{-1}

Experiment 13: Results obtained passing CH$_4$/CO$_2$/O$_2$ mixtures over 50 mg Ni/Al$_2$O$_3$(CRG'F').
GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.
O$_2$ conversions ≥ 99.7%

Feed Composition			% CH$_4$ converted	%CO$_2$ converted	% yield H$_2$	%yield CO
% CH$_4$	% CO$_2$	%O$_2$				
56.7	28.1	15.0	89	83	87	87
56.4	29.2	14.4	85	87	79	85

Experiment 14: Results obtained passing CH$_4$/CO$_2$/O$_2$ mixtures over 50 mg 1% Pt/Al$_2$O$_3$.
GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.
O$_2$ conversions ≥ 99.7%

Feed Composition			% CH$_4$ converted	%CO$_2$ converted	% yield H$_2$	%yield CO
% CH$_4$	% CO$_2$	% O$_2$				
58.2	27.9	13.9	37.5	28.0	25.7	34.5

Experiment 15: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg $Ni/Al_2O_3(CRG'F')$,
GHSV = 2×10^4 hour^{-1}, 1050 K, 0.1 MPa.
O_2 conversions ≥ 99.7%

Feed Composition			% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
% CH_4	% CO_2	% O_2				
15.0	74.7	10.3	99.8	19.2	33.4	32.7
17.2	72.0	10.8	100.0	23.4	25.9	38.2
25.0	65.8	9.2	99.2	40.9	58.3	57.0
34.0	58.1	7.9	97.0	56.3	74.1	52.4
33.0	58.3	8.7	98.0	53.3	73.7	69.4

References

1. All data taken from "Handbook of Chemistry and Physics" 61st ed. (CRC Press, 1980-1981).
2. J. T. Richardson and S. A. Paripatyader, Appl. Catal., 1990, 61, 293.

Claims

1. A method of converting a reactant gas mixture comprising CO_2, O_2 and CH_4 into a product gas mixture comprising H_2 and CO which method comprises bringing the reactant gas mixture at a temperature of from 600 -1000°C into contact with a solid catalyst of at least one metal selected from Ir, Rh, Ru, Pd, Ni and Pt, on a refractory support, characterised in that CO_2, O_2 and CH_4 are all present in the feedstock gas mixture and a single reaction vessel is used.

2. A method according to claim 1, in which the composition of the reactant gas mixture is selected so as to obtain a thermally neutral reaction.

3. A method according to claim 1 or claim 2, wherein the ratio of CO_2 to O_2 is approximately 1:6.

4. A method according to any one of claims 1 to 3 in which the ratio of CO_2(a) and O_2(b) to CH_4 (c) is c= 2b +a .

5. A method according to any one of claims 1 to 3 in which the ratio of CO_2(a) and O_2(b) to CH_4 (c) is a/c - 2b>1.

6. A method according to any one of claims 1 to 5, wherein the combined partial pressure of the reactant gases is from 0.1mPa to 10MPa.

7. A method according to any one of claims 1 to 6, wherein the combined partial pressure of the reactant gases is approximately 0.1 MPa.

8. A method according to any one of claims 1 to 7, wherein the reaction temperature is from 750 to 850°C.